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(57) Abstract

The invention relates to an antiskid medium which comprises a substrate and a deicing agent, the substrate being a porous material made from a natural mineral and the deicing agent being an alkali metal formate or earth alkali formate, such as sodium or potassium formate, which has been introduced into the substrate by impregnation. The invention also relates to a method for the manufacture of this antiskid medium.

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Antiskid medium and a method of preparation of the same

The invention relates to an antiskid medium according to the preamble of Claim 1. The invention also relates to a method for the preparation of this antiskid medium.

Ice formed on the surface of a traffic route is a hazard factor, and efforts are made to prevent it by spreading on the road surface either deicing agents or mediums such as sand which increase the friction of the ice surface. The most common deicing agent is road salt, which in general consists of sodium chloride or calcium chloride. Road salt works in such a manner that the sodium or calcium chloride spread on ice will melt the ice under it, whereby a sodium or calcium chloride solution having a very low freezing point is formed. The more there occurs melting, the more dilute the sodium or calcium chloride will become. Melting will continue until a solution concentration is reached the freezing point of which is the same as the temperature prevailing outdoors. Thereafter the road surface will refreeze. Thus the antiskid effect of road salt will last for only a certain period, whereafter new salting must be carried out. In addition, calcium chloride, and also other chloride-based road salts, have the disadvantages of their corrosive action on vehicles and the environmental problem caused by them in roadside areas.

FI patent application 884 194 discloses a method in which sand or some other substrate particle is coated with a slurry which contains a carboxylate of an earth alkali metal or alkali metal, in particular calcium magnesium acetate. A number of thin layers of slurry are caused to form on the surface of the substrate particle. Conventional pelleting methods are used as the coating method. Such an antiskid medium has the advantage that both a deicing agent and a gritty substance which increases the friction of an ice surface are combined therein. However, there is the disadvantage that the manufacture of such

a medium presupposes a relatively multi-stage manufacturing process. In particular, the spreading of the slurry on the substrate surface presupposes a pelleting-type manufacturing process, which, as is known, is a process step difficult to control and may easily lead to a non-homogenous product. Also, the performance of such a medium has deficiencies. The deicing agent causes the formation of a melted layer, into which the grit will "sink." When the solution freezes, the surface will again be slippery. An ideal antiskid medium should have the capacity to melt the ice underneath and at the same time to cause the antiskid medium to adhere to the ice surface and keep it constantly on the surface.

In the art there is need for producing an antiskid medium which, on the one hand, contains a deicing agent and, on the other hand, a medium which increases friction, in such a manner that the medium is of an even quality and light in weight, and is easy to manufacture. Another object is an antiskid medium with which said "sinking" will not occur. A further object is a medium the use of which will reduce the environmental hazards to road areas and which will not corrode vehicles to the extent road salt does. These objects can be achieved with the antiskid medium according to the invention, which is mainly characterized by the facts stated in the characterizing clause of Claim 1.

The medium according to the invention for use for antiskid purposes comprises a porous substrate impregnated with a solution which contains an alkali or earth alkali metal formate serving as the deicing agent. After impregnation the material is dried, whereupon the deicing agent crystallizes in the pores of the substrate.

The substrate is preferably a particulate material prepared from fired clay, i.e. expanded clay. The raw material of expanded clay is a plastic clay. After preliminary working, the

clay is fired in a rotary kiln at a temperature of approx. 1150 °C. During the firing the clay expands and is molded under the rotary motion into sintered spherical pellets. The pellets are porous and full of small air voids. The particle size of such expanded clay is typically approx. 3-7 mm, and it is capable of adsorbing water at a rate of approx. 10 % of its volume in 10 minutes. The density of the pellets is approx. 0.3-0.5 kg/l, i.e. the pellets will float on water.

The porous substrate may be, for example, in the form of spherical pellets, but it may also be in the form of crushed material. Such crushed material can be prepared by slightly crushing the spherical pellets. The advantage of crushed material is that it has sharp edges, in which case it is a more effective antiskid medium than are spherical pellets.

According to the invention, preferable deicing agents include sodium formate and potassium formate, in particular potassium formate. An aqueous solution of potassium formate has a very low freezing point (at the eutectic point the freezing point is -70 °C), in addition to which the chemical is non-toxic and is not corrosive to the same extent as are, for example, chloride solutions which are known as deicing mediums.

It is a particular advantage of the formates used according to the invention that, when impregnated into a porous substrate, such as expanded clay, they reduce dust emissions from the substrate. This is an advantage, especially at the manufacturing stage of the antiskid medium, at which stage the fine-grained mineral dust, such as silicate dust, emitting from the substrate, such as expanded clay, constitutes an occupational health problem. Also at the stage of spreading the antiskid medium, the reduction of dust emissions into the environment is a significant advantage. For example, by means of sodium or potassium formate the dust emissions from substrate particles can be reduced by 30-40 %. Economy is at its best with a 15 %

solution. Sodium formate is formed as a byproduct in the organic chemical process industry, and its advantages include its low price and commercial availability. It is not very detrimental in its corrosive action, and its toxicity is also low. Potassium formate can be prepared, for example, from carbonate or hydroxide and formic acid. Potassium formate has slightly better antiskid properties than has sodium formate.

The antiskid medium according to the invention contains a deicing agent preferably in an amount of approx. 3-30 % by weight, and especially preferably in an amount of approx. 5-20 % by weight.

The antiskid medium described above can, according to the invention, be manufactured by impregnating the porous material serving as the substrate with an aqueous solution of the deicing agent, whereafter the porous material impregnated with the said solution is dried.

The concentration of deicing agent in the aqueous solution is preferably approx. 10-30 % by weight, and especially preferably approx. 15-25 % by weight.

The impregnation period may vary from 10 minutes to 3 hours. After the impregnation, the excess solution is drained from the porous material on, for example, a sieve mesh, whereafter the porous material is dried. A suitable drying temperature is approx. 30-100 °C, preferably approx. 40-70 °C.

The antiskid medium according to the invention works on an ice surface as follows. Under the action of the deicing agent, the ice beneath the pellet begins to melt, whereupon the pellet will partially sink into the formed depression and at the same time adhere to the ice surface through freezing. At this stage, part of the solution phase is also adsorbed to the pellet. The pellet thus serves as a storage for the deicing agent, which is

released slowly. On the other hand, when a vehicle runs over the pellet, the pellet is crushed and the crushed material will increase the friction of the ice surface.

The invention is described below in greater detail with the help of examples concerning the antiskid properties and dustiness of the material.

Antiskid action

Expanded clay, which is porous fired clay having a particle size within the range 3-7 mm and a volume weight of 0.3 kg/l, was mixed with potassium formate solutions of different concentrations. The same quantity of expanded clay (2.5 kg) was used in each test. Seven different solution concentrations were used in the tests (Table 1). The impregnation was carried out in vats, in which the solution was allowed to impregnate the expanded clay for 2 h. After the impregnation, any excess solution was separated from the pellets by screening, and the pellets were dried in an incubator (50 °C). In tests 1, 2 and 7, the drying period was 4 days, in the other tests it was 2 days. Data on the materials in the tests are compiled in Table 1.

Table 1

Tests of impregnation of expanded clay with potassium formate

Test	Solution, concentration	Wet weight kg	Dry weight kg	Volume weight kg/l
1	72 %	4.3	3.9	0.5
2	50 %	4.1	3.3	0.40
3	30 %	3.8	2.8	0.38
4	25 %	3.5	2.5	0.30
5	20 %	3.9	2.7	0.33
6	15 %	3.7	2.6	0.33
7	10 %	3.3	2.2	0.28
8	-	-	2.5	0.30

Treated and untreated expanded clay pellets were spread onto an ice surface, and their behavior was observed visually and by testing the slipperiness underfoot. The weather during the tests was windy and cloudy.

In tests 1 and 2, the pellets melted the ice beneath them and sank into the ice, whereafter they no longer worked as antiskid media.

In terms of adherence of the pellets, tests 4 and 5 (a 20 % to 25 % solution) yielded the best results. Within an hour the potassium formate had already caused the pellets to adhere to the ice surface through melting.

Untreated pellets became rapidly piled up by wind, and some of the pellets were carried away by wind.

Dust emission

Example 1 (Comparative Example)

Light expanded clay aggregate (Leca) was placed on a sieve, and any loose dust was rinsed off with distilled water. Thereafter the crushed material was dried in an incubator at 105 °C. Approx. 100 g of the dried crushed material was weighed onto a sieve. Thereafter the crushed material was transferred to a 10-liter drum, which was rotated for 15 minutes. The crushed material was poured onto a sieve, and fine dust was screened off. Thereafter the crushed material was weighed. The crushed material was returned to the drum, which was rotated for another 15 minutes, the total period of rotation thus being 30 min. Thereafter the crushed material was screened and weighed. The test was repeated 3 times; the mean result is given in Table 1. According to the results, on average 5.2 g out of a 100 g dried sample turned into dust in the first rotating. After the second rotating on average 10.6 % had turned into dust. In other words, after the first rotating, 5.2 % of the original dried and dust-free mass had turned into dust, and

after the second rotating the corresponding value was 10.6 %. These percentage values were used as reference values in the following examples.

Example 2

The procedure was in other respects the same as in Example 1, but now the sieve-dried and weighed, approx. 100 g sample, together with the sieve, was immersed into a 5 % sodium formate solution for approx. 15 seconds, whereby the crushed material was thoroughly moistened. Thereafter any excess solution was allowed to run off. The sample was dried at 105 °C and was thereafter weighed (100.7 g). The sample was then transferred to a 10-liter drum, which was rotated for 15 minutes. The sample was poured onto a sieve, and any fine dust was screened off. Thereafter the sample was weighed, and the dust amount was calculated; it was 5.1 % of the original mass of the dried material. The sample was returned to the drum, which was rotated for another 15 minutes. Thereafter the sample was screened and weighed. The result obtained was that now in total 10.2 % of the mass had turned into dust.

Examples 3 and 4

The procedure was in other respects the same as in Example 2, but 15 % and 30 % sodium formate solutions were used, and the drying was carried out at 105 °C. The results are shown in Table 1.

Table 1

Results of dust emission tests of Examples 1-4. The amount of dust is indicated in per cent of the original dust-free mass of the crushed material.

Example No.	Solution	Drying °C	Dust amount (%) 15 min	30 min	Adsorbed salt amount (%)
1	Reference	105	5.2	10.6	-
2	HCOONa 5 %	"	5.1	10.2	0.7
3	HCOONa 15 %	"	3.0	7.2	1.8
4	HCOONa 30 %	"	3.0	6.7	4.1

From the results in Table 1 it can be concluded that by means of sodium formate the amount of dust can be reduced at best by 30-40 %. Economy is at its best when a 15 % solution is used.

Example 5 (Comparative example)

Dust emission tests were carried out by using a larger batch of expanded clay. A batch of 2.370 kg was weighed of an expanded clay from which any loose dust had been screened off by using a Sweco sieve. The pellets were placed in a concrete mixer, which was rotated for 10 minutes. Any loose dust was screened off from the pellets, and the pellets were weighed, whereupon the result obtained was that the mass had been reduced by 6.1 %. Thereafter, rotation in the concrete mixer was continued for 5 min (in total 15 min), whereafter the pellets were screened and weighed. The result obtained was that after 15 minutes of rotation the mass of the pellets had been reduced by 9.0 %. Thereafter, rotation was continued for a further 15 min (total period 30 min), whereupon, upon weighing, the mass of the pellets had been reduced by a total of 17 %. These percentage values were used as reference values in the following Example 6.

Example 6

The procedure was otherwise the same as in Example 5, but now

the weighed amount of pellets was poured into a bucket containing a 15 % solution of sodium formate. Thereafter the moistened expanded clay was poured onto a sieve to drain and was dried at 105 °C. After the drying, the pellets were weighed and placed in a concrete mixer, in which they were rotated for 10 min, thereafter for 5 min, and finally for 15 min. After rotation, screening and weighing were carried out. The result obtained was that after 10 minutes the mass had been reduced by 3.2 %, after 15 minutes by 5.6 %, and after 30 minutes by 12.0 %. The results are shown in Table 2.

Table 2

Results of dust emission tests carried out in a concrete mixer. The dust amount is indicated in per cent of the original dust-free mass of the pellets.

Example No.	Solution	Drying °C	Dust amount (%) 10 min	15 min	30 min	Adsorbed salt amount (%)
5	Reference	105	6.1	9.0	17,0	-
6	HCOONa 5%	"	3.2	5.6	12.0	2.8

Above, dust emission results for Na formate are shown. It is clear that dust emissions are also reduced when K formate is used instead of, or in addition to, Na formate. Earth alkali metal formates, such as Ca and Mg formate, also behave in a very similar manner.

Claims

1. An antiskid medium which comprises a substrate and a deicing agent, **characterized** in that the substrate is a particulate porous material made from a natural mineral and that the deicing agent is an alkali metal formate or earth alkali metal formate which has been introduced into the substrate by impregnation.

2. An antiskid medium according to Claim 1, **characterized** in that the deicing agent is sodium formate or potassium formate, in particular potassium formate.

3. An antiskid medium according to Claim 1 or 2, **characterized** in that the density of the porous material is approx. 0.3-0.5 kg/l.

4. An antiskid medium according to any of the above claims, **characterized** in that the porous material is expanded clay.

5. An antiskid medium according to any of the above claims, **characterized** in that the particle size of the porous material is approx. 3-7 mm.

6. An antiskid medium according to any of the above claims, **characterized** in that it contains the deicing agent in an amount of approx. 3-30 % by weight, preferably approx. 5-20 % by weight.

7. A method for the manufacture of an antiskid medium according to any of the above claims, **characterized** in that the porous material serving as the substrate is impregnated with an aqueous solution of the deicing agent, whereafter the porous material impregnated with the said solution is dried.

8. A method according to Claim 7, **characterized** in that the concentration of the deicing agent in the aqueous solution is approx. 10-30 % by weight, preferably approx. 15-25 % by weight.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 96/00367

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C09K 3/18
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0301337 A1 (CANZANI, ALBERTO), 1 February 1989 (01.02.89), page 3, line 17 - line 19, claims 2, 11, abstract --	1-8
Y	EP 0375214 A1 (BP CHEMICALS LIMITED), 27 June 1990 (27.06.90), claims 1,3, abstract -- --------	1-8

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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